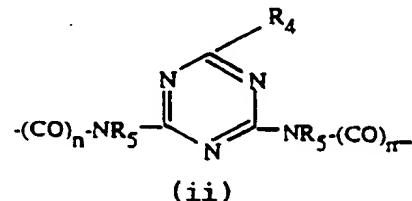
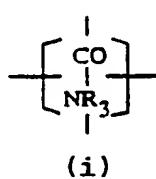
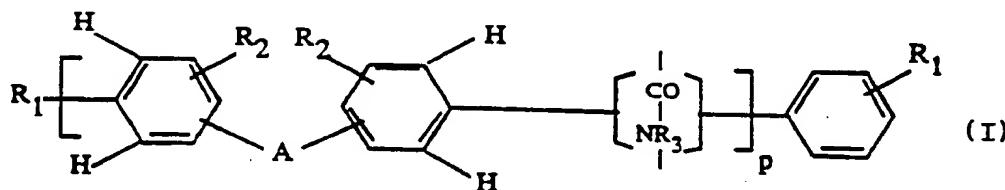




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08G 69/00, 69/48	A1	(11) International Publication Number: WO 91/03511 (43) International Publication Date: 21 March 1991 (21.03.91)
(21) International Application Number: PCT/EP90/01495		(74) Common Representative: SANDOZ LTD; Lichtstrasse 35, CH-4002 Basel (CH).
(22) International Filing Date: 6 September 1990 (06.09.90)		
(30) Priority data: P 39 30 089.7 9 September 1989 (09.09.89) DE P 39 32 912.7 3 October 1989 (03.10.89) DE		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.
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(54) Title: SYNTHETIC POLYAMIDES AND THEIR SALTS



(57) Abstract

A synthetic polyamide of formula (I) and its salts in which each R₁ independently is selected from hydrogen, carboxyl, amino or a group of formula (α): -A₁-R₁₀ where A₁ is a bridging group and R₁₀ is a sterically hindered amine group; each R₂ independently is hydrogen or a group of formula (α); A is a bridging group of formula (i) or (ii); n is 0 or 1; R₃ is hydrogen, C₁₋₁₂alkyl or is a significance of R₁₀; R₅ is hydrogen or C₁₋₁₂alkyl; R₄ is a significance of R₁₀ or a group of formula (α); and p is an integer from 5 to 200; with the proviso that the compound of formula (I) contains 1-400 sterically hindered amine groups.

* See back of page

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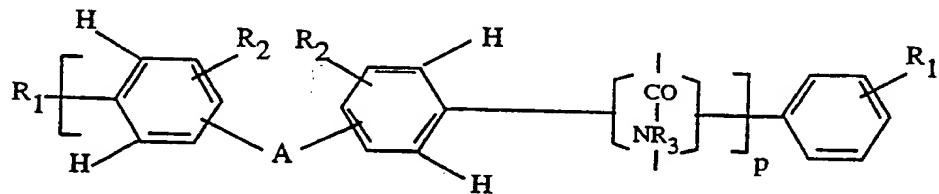
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SYNTHETIC POLYAMIDES AND THEIR SALTS

The invention relates to synthetic polyamide of aromatic character and their salts containing sterically hindered amine groups which are not part of the polyamide recurring backbone but are in a side chain attached to the said backbone.

According to the invention there is provided a compound of formula I



in which each R₁ independently is selected from hydrogen, carboxyl, amino or a group of formula α

-A₁-R₁₀

(α)

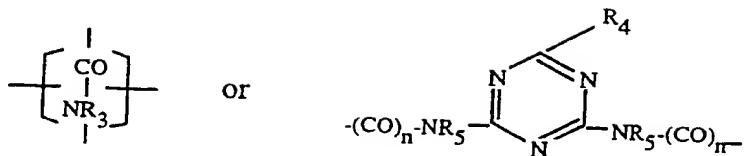
where A₁ is a bridging group and R₁₀ is a sterically hindered amine group;

each R₂ independently is hydrogen or a group of formula α (preferably hydrogen);

A is a bridging group of the formula

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n is 0 or 1;

R_3 is hydrogen, C_{1-12} alkyl or is a significance of R_{10} , independent of R_{10} (preferably hydrogen),

R_5 is hydrogen or C_{1-12} alkyl (preferably hydrogen) and

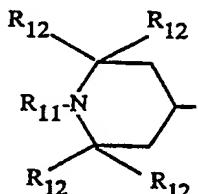
R_4 is a significance of R_{10} , independent of R_{10} , or a group of formula α , and

p is an integer from 5 to 200 (preferably 10-100, more preferably 10 to 30),

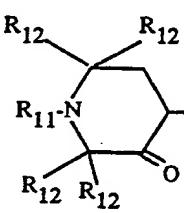
with the proviso that the compound of formula I contains 1-400 (preferably 2 to 100, more preferably 2 to 30) sterically hindered amine groups.

In this Specification where a symbol appears more than once in a formula, its significances are independent of one another unless indicated to the contrary.

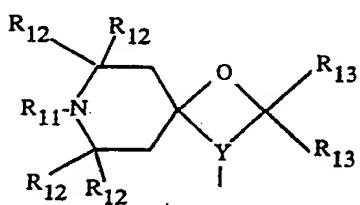
In this specification, preferably any R_{10} independently is R_{10}' where R_{10}' is a group of formula a to e



(a)



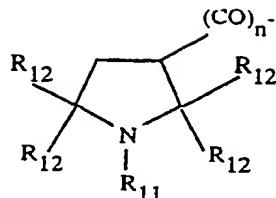
(b)



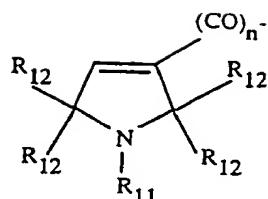
(c)

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(d)



(e)

in which R_{11} is hydrogen or C_{1-4} alkyl, preferably hydrogen or C_{1-2} alkyl;

each R_{12} independently is C_{1-5} alkyl (preferably methyl),

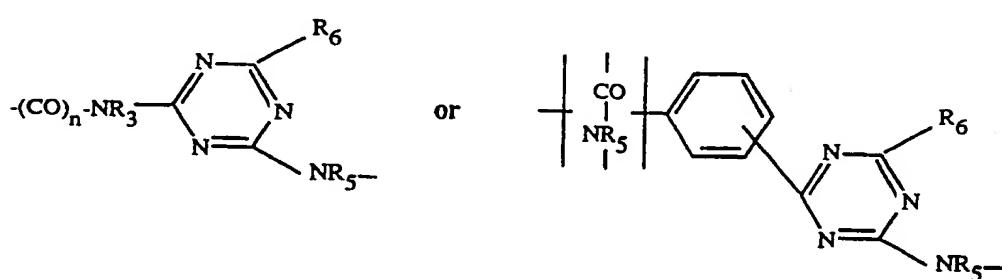
each R_{13} independently is hydrogen, C_{1-2} alkyl or one group R_{13} is phenyl and the other R_{13} is hydrogen or C_{1-2} alkyl or both groups R_{13} together form a group of the formula $-(CH_2)_{11}-$;

n is 0 or 1 and

Y is $-N-CO-$ or $-CO-N-$.

More preferably R_{10} is a group of formula a) most preferably when R_{11} is hydrogen or methyl and R_{12} is methyl.

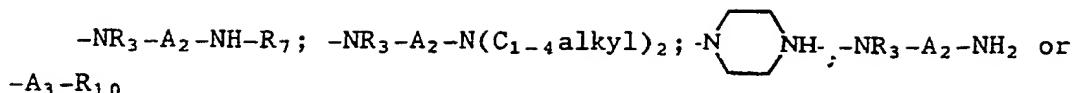
Preferably A_1 is A_1' where A_1' is $-NR_5-$, $-CO-NR_5-$, $-NR_5-CO-$ or $-O-CO-$ (where $CO-$ is attached to the benzene) $-NR_5-\text{C}_6\text{H}_4-NR_5-$, $-NR_5-\text{CH}_2-\text{CO}-NR_3-$ (where NR_5 is attached to the benzene)



(in which R_{10} is attached to $-NR_5-$),

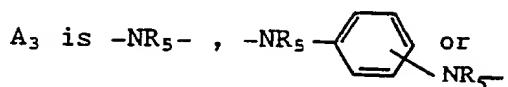
where R_6 is a group of the formula

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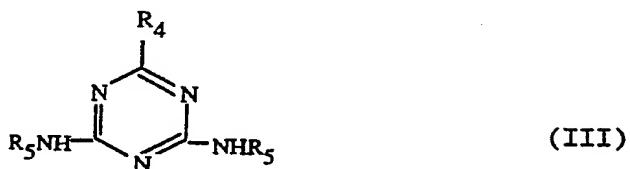
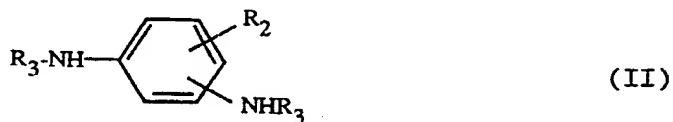
where A_2 is C_{1-6} alkylene

R_7 is C_{1-4} alkyl

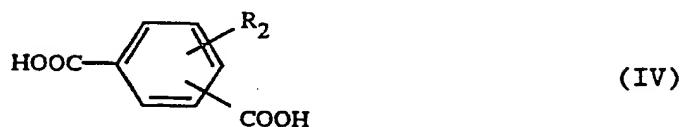


$-\text{NR}_3-\text{A}_2-\text{NR}_5-$.

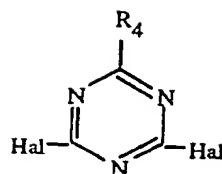
Compounds of formula I can be prepared by reacting one mole of a compound of formula II or III



or a mixture of these compounds with one mole of a compound of formula IV or V



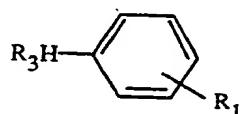
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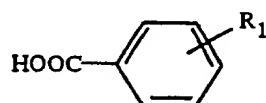
(V)

or a mixture of these compounds (where in the place of the free acids the acid halides are preferably used), wherein the groups R₂ and/or R₃ contain at least 1 sterically hindered amino group.

The chain length of the new compounds according to the invention can be regulated by introducing amounts of appropriate monofunctional compounds of formula VI or VII or α



(VI)



(VII)

or by regulating the amount of compounds used from which groups a) to e) above are derived. Such regulation is well known to a man skilled in the art.

Compounds of formula I according to the invention, both those with a high hindered amine content and those with a low hindered amine content per repeating unit can be used as coatings or spun to form fibers or threads which can be made into fabrics and knitted to make goods and can be dyed with anionic dyestuffs (particularly those known to be suitable for dyeing synthetic polyamide material). The compounds containing a high content of hindered amines may also be used for salt formation when mixed with a required amount of dyestuff, or an optical brightener or another stabiliser. As such these compounds are mixed, preferably in the form of a solution (e.g. in

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dimethylacetamide) with unmodified aromatic polyamide (e.g. "Nomex" by Du Pont).

The resulting polyamide has good fastness to light, oxidation and to heat, as well as having good wet fastness properties.

The soluble polyamide can be used for example in lacquers and in printing inks, where they will tend to increase the light stability.

Further according to the invention there are provided a polymeric composition comprising a compound of formula I and a different polymeric material.

Preferably 1 to 10%, (more preferably 2 to 5%) of the compound of formula I is present in such a polymeric composition, all weights being based on the weight of the total composition. Such compositions can be used as plastic materials or in printing inks or lacquers.

In the preparation of carrier material for chromatography or for peptide synthesis, the amount of sterically hindered groups can vary greatly. The retention properties of the compounds of formula I (preferably when used in powder or granulated form) are good.

The new compounds according to the invention can be easily dyed with anionic dyestuffs both in the mass as well as by exhaustion dyeing and can be used in small amounts to produce a good dyeing of plastics, in particular aromatic polyamide which until recently has been very poorly dyeable. The dyeings produced on such polyamide show good light fastness, good heat and wet fastness properties as well as improved stability of the dyed substance against light, heat and oxidation. The compounds of formula I with sterically hindered amines have good migration fastness. Further the new compounds according to the invention can act as a material for chromatographic purposes and polypeptides synthesis, in particular for high performance chromatographic systems and as a media for separation of biomolecules from non-biomolecules.

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Compounds of the formula I are particularly reactive towards anionic optical brighteners or with anionic plastics stabilisers, for example UV stabilisers such as sulfonated 2(2-hydroxyphenyl) benztriazoles or 2-hydroxybenzophenones. The compounds of formula I can be reacted with acid dyestuffs and with optical brighteners and the stabilisers as mentioned above to form salts of such products. Such salts can be mixed with polyamide. Such a salt can be added in the usual amounts for example for plastics 0.05 to 10% preferably 0.1 to 5% by weight based on the amount of plastics composition.

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The invention will now be illustrated by the following Examples, in which the parts are parts by weight and all temperatures are in °C.

Example 1

872 parts of N-methylpyrrolidone are poured into a 1.5l reaction vessel.

28.35 parts (0.2625 moles) of 1,4-diaminobenzene are added at 20°C +/- 2°. The mixture is cooled to 0° and 50.75 parts (0.25 mole of benzene 1,4-dicarboxylic acid dichloride (terephthaloyl dichloride) are added portion by portion stirring well and at a constant temperature.

After this, the mixture is heated for 4 hours in stages from 20 to 80°C.

5.3 parts (0.125 moles) of 2-chloro-4,6-bis-(2',2',6',6'-tetramethyl piperidyl-4'-amino)-triazine are added and the mixture is stirred for 4 hours at 100°C. The resulting precipitate is separated by filtration and washing with water from the liquid phase and is dried at 100°C under vacuum of 20mm Hg.

66 parts of a light beige powder results with improved properties, for example improved dyeability.

Further compounds according to the invention can be made by reacting 0.2625 moles of the compound in column I of Table 1 with 0.25 moles of the compound of column II of Table 1 and 0.125 moles of the chloro compound of column III of Table 1.

R₆₀ in the following Tables is the group 2,2,6,6-tetramethylpiperidyl-4 and R₇₀ is 1,2,2,6,6 pentamethyl piperidyl-4.

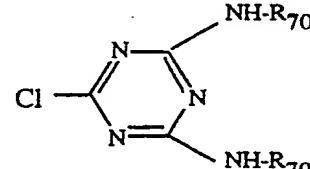
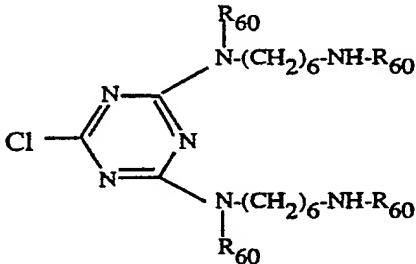
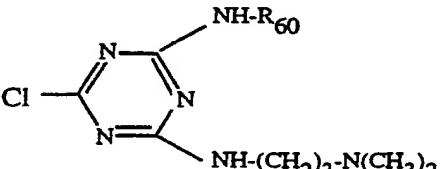
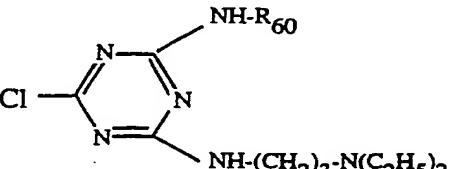
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TABLE 1

Ex	I	II	III
2	1,3-Diamino- benzene	benzene-1,3 dicarboxylic acid dichloride	2-Chloro-4,6-(2',2',6',6',- tetramethylpiperidyl-4- amino)-triazine
3	do.	do.	
4	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
5	1,3-Diamino- benzene	benzene-1,3-dicarboxylic acid dichloride	do.
6	do.	do.	
7	do.	do.	
8	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
9	do.	do.	
10	1,3-Diamino- benzene	benzene-1,3-dicarboxylic dichloride	do.

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Table 1 (cont)

<u>Ex</u>	<u>I</u>	<u>II</u>	<u>III</u>
11	do.	do.	
12	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
13	do.	do.	Cl-CH ₂ -COHN-R ₆₀
14	1,3-Diamino- benzene	benzene-1,3-dicarboxylic acid dichloride	do.
15	do.	do.	
16	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
17	do.	do.	
18	1,3-Diamino- benzene	benzene-1,3-dicarboxylic acid dichloride	do.
19	do.	do.	
20	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.

Example 21-39

872 parts N-methylpyrrolidone is poured into a 1.5 liter reaction vessel at 20°C +/- 2°C. 27.0 parts (0.25 moles) of 1,4-diaminobenzene are dissolved therein and then, at 0°C, 51 parts (0.25125 moles) of benzene-1,4-dicarboxylic acid dichloride are added. Over 4 hours the temperature is brought, in stages, from 20°C to 80°C and 0.3 parts (0.0125 moles) of 1-amino-4-(2',2',6',6'-tetramethylpiperidinyl-4'-amino)-benzene are added and the mixture is stirred for 4 hours at 100°C. The resulting solid is then filtered at 100°C washed with water at 20°C and dried at 100°C under 20mm Hg.

61.3 parts of a modified polyamide with improved properties results.

Further modified polyamides can be made according to Example 1 using 0.25 moles of the amine of column I with 0.25125 moles of the compound of column II and 0.0125 moles of the amino compound of column III of Table 2.

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Table 2

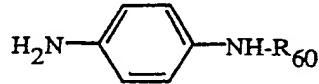
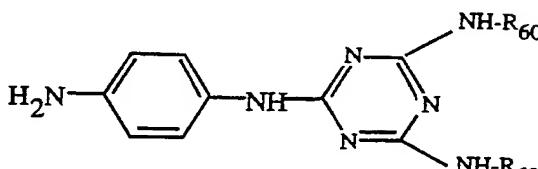
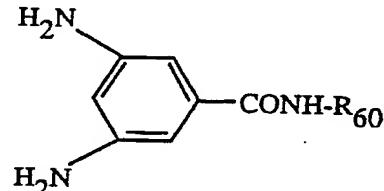
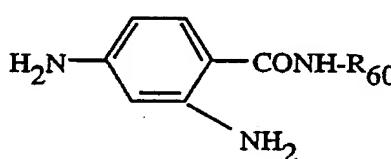
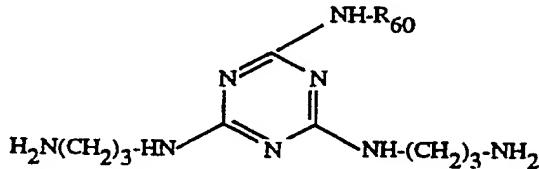
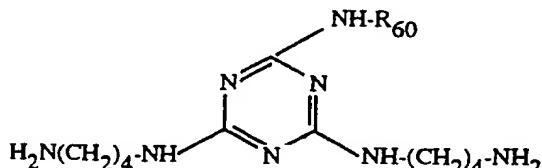
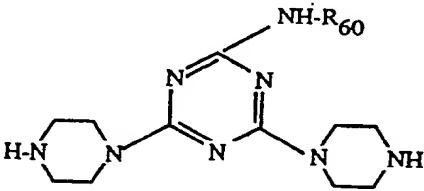
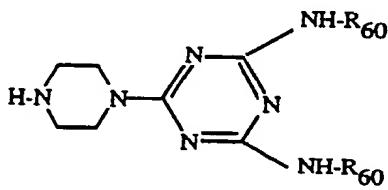
Ex	I	II	III
22	1,3-Diamino- benzene	benzene-1,3-dicarboxylic acid dichloride	
23	do.	do.	
24	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
25	do.	do.	
26	1,3-Diamino- benzene	benzene-1,3-dicarboxylic acid dichloride	do.
27	do.	do.	
28	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
29	do.	do.	

Table 2 (cont)

Ex	I	II	III
30	1,3-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
31	do.	do.	
32	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.
33	do.	do.	
34	1,3-Diamino- benzene	benzene-1,3-dicarboxylic acid dichloride	do.
35	do.	do.	
36	1,4-Diamino- benzene	benzene-1,4-dicarboxylic acid dichloride	do.

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Example 37

98 parts of a nylon 6 granulate are mixed with 2 parts of the product of Example 1 in a powder mixer (Rhoenrad) for 1 hour and then are extruded using a laboratory extruder (Type MARIS TM 33 V/32 D) under the following conditions and then are spun.

Speed of the screw	321 rpm
Rate of dosage	40%
Yield	23 kg/hour
Pressure	2 bars
Temperature in Zones	1 2 to 6 7 8 and 9 168° 300° 259° 263°

The resulting fibers can be used as such or can be worked into fabric knitted goods, or yarns which is usual for polyamide fiber materials.

Example 37 can be repeated using instead of the product of Example 1, 2 parts of the product of any one of the Examples 2-36.

The resulting polyamide material can be dyed with acid dyes for example with the following dyestuffs;

C.I. Acid Red 216
C.I. Acid Violet 66
C.I. Acid Yellow 155
C.I. Acid Blue 230,
C.I. Acid Red 129,
C.I. Acid Red 184,
C.I. Acid Red 119, or
C.I. Acid Blue.

The resulting dyeings show a good depth of color (comparable to the same dyeing on non-modified polycaprolactam) and have a good brilliance and have good light and wash fast properties.

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Example 38

14.5 parts of 3,5 diaminobenzoic acid-2',2',6',6'-tetramethyl-piperidyl-4-amide (produced by the condensation of 3,5-dinitrobenzoic acid with 2,2,6,6-tetramethyl-4-aminopiperidyl and reduction of the nitro groups) are dissolved in 206 parts of anhydrous N-methyl-pyrrolidone. The solution is cooled to a temperature of 0 to 5° and 10.15 parts isophthalic acid dichloride are added portion by portion within 1 hour. The resultant mixture is stirred for 2 hours at 20-25° and then for 6 hours at 100°. The N-methyl-pyrrolidone is then distilled off under vacuum. The viscous mass is then stirred in 250 parts of acetone and a light beige precipitate forms which is separated by filtration. The residue is stirred in 200 parts of 2% sodium hydroxide at room temperature filtered then washed neutral in 200 parts of water in four portions and dried at 80° under vacuum of about 50 Pa. The molecular weight of the resulting polyamide is about 6,400 having a melting point of over 300°.

Example 39

A very similar product to that obtained according to Example 38 is produced, when in the place of 14.5 parts 3,5-diaminobenzoic acid-(2',2',6',6',-tetramethylpiperidyl-4')-amide 3,5-diaminobenzoic acid-1',2',2',6',6',-pentamethylpiperidyl-4'-amide is used.

Examples 40 and 41

According to the method of Example 38, 12.35 parts of 4-(2',2',6',6',-tetramethylpipieridyl-4'-amino)-aniline (produced by condensation of para-chloro-nitrobenzene with 2,2,6,6,-tetramethyl-4-aminopiperidine and reduction of the nitro group) or 13.05 parts of 4-(1',2',2',6',6',-pentamethylpiperidyl-4'-amino)-aniline are reacted with 10.15 parts of isophthalic acid dichloride. The resulting products are very similar to those obtained in Examples 38 and 39.

Example 42 to 45

The reactions according to Examples 38 to 41 are repeated, but in the place of isophthalic acid dichloride the same quantity of terephthalic acid dichloride is used. The resulting products are very similar to those of Examples 38 to 41.

Example 46

98 parts of a commercial soluble aromatic polyamide poly-metaphenylene-isophthalamide ("Nomex" from Du Pont) are mixed with 2 parts of the product of Example 38, dissolved in 400 parts dimethylacetamide and spun into fibers, according to known methods. The resulting fibers can be dyed, by exhaustion, with 1 part (ca. 1% dyeing) of the dyes listed in Example 37. The resulting deep dyeings are very brilliant and fast to washing, light and oxidation.

Example 47

14.5 parts of 3,5 diaminobenzoic acid-2',2',6',6'-tetramethyl-piperidyl-4-amide (produced by the condensation of 3,5-dinitrobenzoic acid with 2,2,6,6-tetramethyl-4-aminopiperidyl and reduction of the nitro groups) are dissolved in 206 parts of anhydrous N-methyl-pyrrolidone. The solution is cooled to a temperature of 0 to 5° and 10.15 parts isophthalic acid dichloride are added portion by portion within 1 hour. The resultant mixture is stirred for 2 hours at 20-25° and then for 6 hours at 100°. The N-methyl-pyrrolidone is then distilled off under vacuum and the viscous residue together with 35.75 parts of C.I. Solvent Yellow 83, (sodium salt) is dispersed in 500 parts of water, stirred for 10 hours at room temperature filtered, washed with water and dried under vacuum at 100°. The resulting dye salt may then be used for dyeing synthetic polyamides of the Aramid type as follows:

A solution of 20 parts of poly-meta-phenylene-isophthalamide ("Nomex" of Du Pont) and 0.5 part of the dye salt in 85 parts of

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dimethylacetamide is spun under known conditions into fibers, which is a brilliant yellow dyeing that is fast to light and washing.

Example 48

Example 47 is repeated using instead of 35.75 parts of C.I. Solvent Yellow 83, 16.35 parts of the sodium salt of 2-(2'-hydroxy-3-sulfo-5'-methylphenyl)-benzotriazole (for additionally improving the light fastness). A fabric results which is extremely fast to light, UV-radiation and weathering.

Example 49

Example 47 is repeated, using instead of 35.75 parts of C.I. Solvent Yellow 83, 20.35 parts of 1-(4'-sulphophenyl)-3-(4"-chlorophenyl)-2-pyrazoline (an optical brightener). This results in a fabric, the brightening aspect of which is very fast to washing and to light exposure.

Example 50

11.2 parts of 5-(1',2',2',5',5'-pentamethylpyrrolidyl-3'-carbonylamino)-isophthalic acid dichloride are added slowly under stirring, into a solution of 5.4 parts of para-phenylenediamine in 150 parts of N-methyl-pyrrolidone at 0 to 5° whilst cooling. Stirring is then continued for 2 hours at room temperature and for 6 hours at 100°. The resulting viscous mass is further treated and used as described in Examples 38 and 46 to 49.

Example 51

Example 50 is repeated using in the place of 11.2 parts of the pyrrolidyl-containing compound, 11.1 parts of 5-(1',2',2',5',5'-pentamethylpyrrolinyl-3'-carbonylamino)-isophthalic acid dichloride may be reacted. The resulting compound is very similar to that of Example 50.

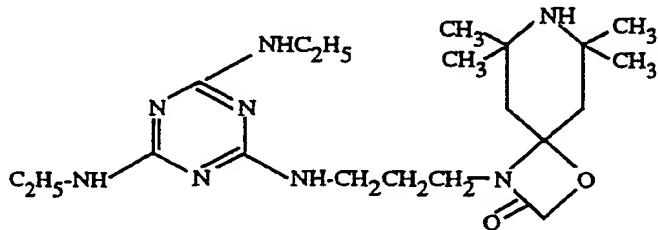
Example 52

16.2 parts of 2,4-diethylamino-6-(2',2',6',6'-tetramethyl-piperidyl-4'-oxy)-triazine are dissolved in 240 parts of N-methyl-pyrrolidone and the solution cooled to 0-5°. Whilst stirring, 10.5 parts of terephthalic acid dichloride are added over 1 hour. Stirring is continued for 2 hours at about 20° and for 6 hours at 100°. The resulting polyamide may be used for enabling the dyeability of aromatic polyamides made with terephthalic acid ("Kevlar" of Du Pont) to be improved or, as such, in powder-form as a chromatographic substance.

2,4-Diethylamino-6-(2',2',6',6',-tetramethylpiperidyl-4-oxy)-triazine is produced by condensation of 1 mol of trichlorotriazine with 2 mol aminoethane and 1 mol 2,2,6,6-tetramethyl-4-hydroxypiperidine.

Example 53

Example 52 is repeated using in place of 2,4-diethylamino-6-(2',2',6',6'-tetramethylpiperidyl-4-oxy)-triazine an equimolecular amount of a compound of formula



A product similar to that of Example 52 results.

Example 54

Example 52 is repeated using 18.95 parts of 2,4-Bis-(2',2',6',6'-tetramethylpiperidyl-4-amino)-6-(2",2",6",6"-tetramethylpiperidyl-4-oxy)triazine in the place of 16.2 parts 2,4-diethylamino-6-(2',2',6',6'-tetramethylpiperidyl-4-oxy)-triazine. An extremely active compound for chromatography is obtained.

Example 55

13.2 parts of 2,4-diamino-5-(2',2',6',6'-tetramethylpiperidyl-4-amino)-benzene are condensed with 10.15 parts of isophthalic acid dichloride according to the method of Example 38. The resulting product is also a very useful compound for chromatography and for preparing dye salts with acid dyestuffs, further stabilisers or optical brighteners.

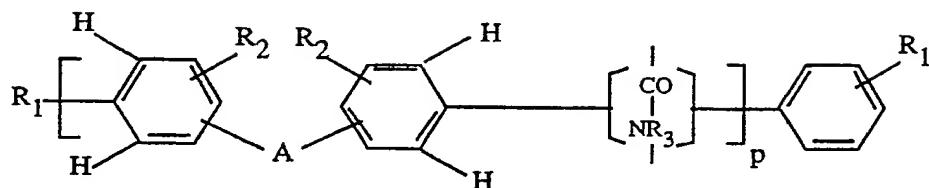
Example 56

Example 55 is repeated using 13.25 parts of 2,4-diamino-5-(2',2',6',6'-tetramethylpiperidyl-4-oxy)benzene in the place of the 13.2 parts of the diaminobenzene. A product with similar properties is obtained.

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Claims:

1. A compound of formula I and its salts



in which each R₁ independently is selected from hydrogen, carboxyl, amino or a group of formula α

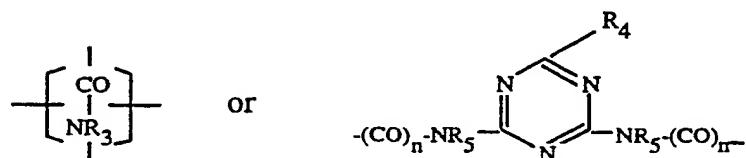
$-A_1-R_{10}$

(α)

where A₁ is a bridging group and R₁₀ is a sterically hindered amine group;

each R₂ independently is hydrogen or a group of formula α

A is a bridging group of the formula



n is 0 or 1;

R₃ is hydrogen, C₁₋₁₂alkyl or is a significance of R₁₀;

R₅ is hydrogen or C₁₋₁₂alkyl;

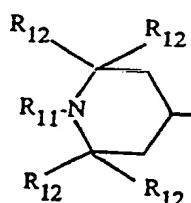
SUBSTITUTE SHEET

R_4 is a significance of R_{10} or a group of formula α ; and

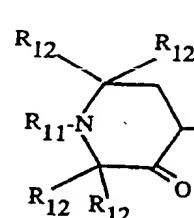
p is an integer from 5 to 200;

with the proviso that the compound of formula I contains 1-400 sterically hindered amine groups.

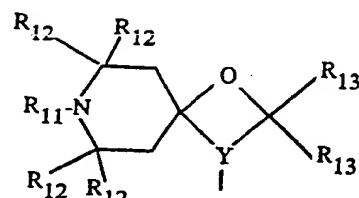
2. A compound according to Claim 1 in which each R_{10} independently is R_{10}' where R_{10}' is a group of formula a to e



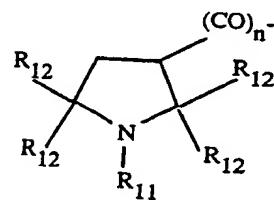
(a)



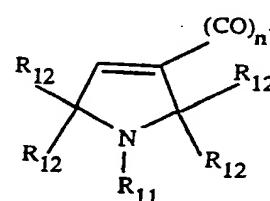
(b)



(c)



(d)



(e)

in which R_{11} is hydrogen or C_{1-4} alkyl;

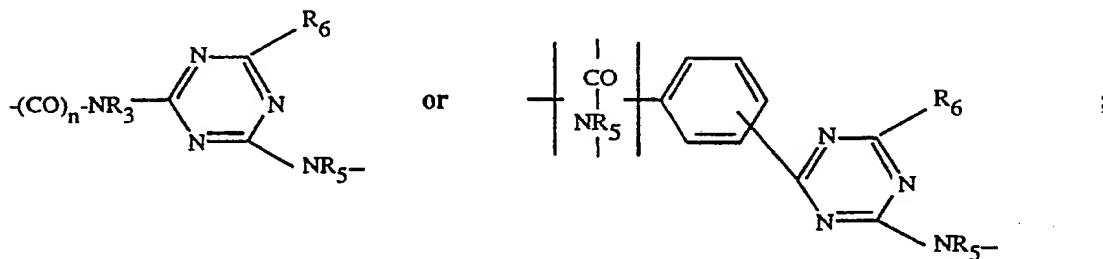
each R_{12} independently is C_{1-5} alkyl;

each R_{13} independently is hydrogen, C_{1-2} alkyl or one group R_{13} is phenyl and the other R_{13} is hydrogen or C_{1-2} alkyl or both group R_{13} together form a group of the formula $-(CH_2)_{11}-$ and

Y is $-N-CO-$ or $-CO-N-$.

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3. A compound according to claim 1 or claim 2 in which A_1 is A_1' where A_1' is $-NR_5-$, $-CO-NR_5-$, $-NR_5-CO-$, $-O-CO-$ (where CO- is attached to the benzene) $-NR_5-$  $-NR_5-$, $-NR_5-CH_2-CO-NR_3-$ (where NR_5 is attached to the benzene)



(in which R_{10} is attached to $-NR_5-$),

where R_6 is a group of the formula

$-NR_3-A_2-NH-R_7$; $-NR_3-A_2-N(C_{1-4}\text{alkyl})_2$;  $-NR_3-A_2-NH_2$ or
 $-A_3-R_{10}$

where A_2 is $C_{1-6}\text{alkylene}$

R_7 is $C_{1-4}\text{alkyl}$

A_3 is $-NR_5-$, $-NR_5-$  or

$-NR_3-A_2-NR_5-$; and

n is 0 or 1.

4. A compound according to any one of the preceding claims in which R_2 is hydrogen.

5. A polymeric compound substantially as herein described with reference to any one of Examples 1 to 56.

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6. A polymeric composition comprising a compound according to any one of the preceding claims and a different polymeric material.
7. A polymeric compound according to claim 6 in which the amount of the composition according to any one of claims 1 to 5 present is 1-10% based on the amount of the polymeric composition.
8. A polymeric composition according to claim 7 in which the amount is 2 to 5%.
9. A polymeric composition according to any one of claims 6 to 8 which is a plastics material or a printing ink or a lacquer.
10. A polymeric composition substantially as herein described with reference to Example 39.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 90/01495

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C08G69/00 ; C08G69/48

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1. 5	C08G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 237 (C-305)(1960) 24 September 1985, & JP-A-60 094457 (MATSUSHITA DENKO K.K.) 27 May 1985, see the whole document ---	1-10
A	EP,A,79406 (JOHNSON & JOHNSON PRODUCTS INC.) 25 May 1983 see claims 1-6 ---	1-10
A	DE,A,1935632 (SANDOZ AG) 23 December 1970 see claims 1, 2 ---	1-10

¹⁰ Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

¹¹T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

¹²X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

¹³Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

¹⁴& document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

1 13 NOVEMBER 1990

Date of Mailing of this International Search Report

28.11.90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

GLANDDIER A

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9001495

SA 39845

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EUDP file on
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13/11/90

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-79406	25-05-83	None		
DE-A-1935632	23-12-70	BE-A- 752017 FR-A, B 2046944 NL-A- 7008471		16-11-70 12-03-71 22-12-70

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